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Rhodium(II)-Catalyzed Stereoselective Synthesis of Allylsilanes

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ABSTRACT

The rhodium-catalyzed decomposition of 2-(triisopropylsilyl)ethyl aryl- and vinyldiazoacetates results in the stereoselective formation of *Z*-allylsilanes. The transformation is considered to proceed by silyl-directed intramolecular C–H functionalization to form a β-lactone intermediate followed by a silyl-activated extrusion of carbon dioxide.

Allylsilanes represent a privileged class of reagents in organic synthesis. They undergo a wide variety of chemical transformations[1,2] and have been used extensively as building blocks in the synthesis of complex molecules.[3] As such, there are many methods for the synthesis of allylsilanes.[4,5] As with any alkene, the preparation of allylsilanes of defined geometry can be challenging. New, complementary methods for the stereoselective generation of allylsilanes are therefore desirable. Herein we describe a stereoselective synthesis of *Z*-allylsilanes by means of rhodium-catalyzed reactions of 2-(triisopropylsilyl)ethyl aryl- and vinyldiazoacetates.

Recently, while investigating the use of 2-(trimethylsilyl)-ethyl diazoacetate **1a** in carbenoid transformations, we observed an unexpected product, allylsilane **2a** (Scheme 1), formed in 29% yield as an 80:20 mixture of *Z*/*E* alkene isomers with $Rh_2(S\text{-DOSP})_4$ as the catalyst. While rhodium-carbenoid chemistry has been used previously to prepare allylsilanes by Si–H insertion,[6,2a] the potential utility of a novel method for the synthesis of allylsilanes led us to explore the reaction further.

We first examined the influence of a variety of rhodium catalysts (Table 1) and found that the catalyst has a marked effect on both the yield and the *Z*/*E* ratio of the allylsilane products. The somewhat bulky chiral catalysts (entries 1–3) gave moderate *Z*/*E* ratios (74:26 to 83:17) and moderate yields (42–57%). The majority of achiral catalysts (entries 4–8) showed essentially no stereochemical preference and gave low to moderate yields of the product. The one exception was the bulky catalyst, rhodium(II) tetrakis(triphenylacetate),[7] $Rh_2(TPA)_4$ (entry 9), which gave the allylsilane **2a** with a *Z*/*E* ratio of 84:16 and in 70% yield. With this catalyst, the optimal conditions were

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(1) For reviews, see: (a) Brook, M. A. *Silicon in Organic, Organometallic and Polymer Chemistry*; Wiley Interscience: New York, 2000. (b) Fleming, I. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, pp 563–593. (c) Sarkar, T. K. In *Science of Synthesis, Houben-Weyl Methods of Molecular Transformations*; Georg Thieme Verlag: Stuttgart, 2001; Vol. 4, pp 901–918. (d) Chan, T. H.; Wang, D. *Chem. Rev.* **1995**, 1279–1292. (e) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293–1316.

(2) For some recent examples, see: (a) Wu, J.; Chen, Y.; Panek, J. S. *Org. Lett.* **2010**, *12*, 2112–2115. (b) Grote, R. E.; Jarvo, E. R. *Org. Lett.* **2009**, *11*, 485–488. (c) Kinnaird, J. W. A.; Ng, P. Y.; Kubota, K.; Wang, X.; Leighton, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 7920–7921. (d) Panek, J. S.; Yang, M. *J. Am. Chem. Soc.* **1991**, *113*, 9868–9870.

(3) For reviews, see: (a) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375–1408. (b) Chabaud, L.; James, P.; Landais, Y. *Eur. J. Org. Chem.* **2004**, 3173–3199.

(4) For reviews, see: (a) Sarkar, T. K. In *Science of Synthesis, Houben-Weyl Methods of Molecular Transformations*; Georg Thieme Verlag: Stuttgart, 2001; Vol. 4, pp 837–900. (b) Sarkar, T. K. *Synthesis* **1990**, 1101–1111.

(5) For some recent methods, see: (a) Takeda, M.; Shintani, R.; Hayashi, T. *J. Org. Chem.* **2013**, *78*, 5007–5017. (b) Ito, H.; Horita, Y.; Sawamura, M. *Adv. Synth. Catal.* **2012**, *354*, 813–817. (c) McLaughlin, M. G.; Cook, M. J. *J. Org. Chem.* **2012**, *77*, 2058–2063. (d) Selander, N.; Paasch, J. R.; Szabó, K. J. *J. Am. Chem. Soc.* **2011**, *133*, 409–411.

(6) (a) Wu, J.; Panek, J. S. *J. Org. Chem.* **2011**, *76*, 9900–9918. (b) Davies, H. M. L.; Hansen, T.; Rutberg, J.; Bruzinski, P. R. *Tetrahedron Lett.* **1997**, *38*, 1741–1744. (c) Bulugahapitiya, P.; Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *J. Org. Chem.* **1997**, *62*, 1630–1641.

(7) Hashimoto, S.; Watanabe, N.; Ikegami, S. *Tetrahedron Lett.* **1992**, *33*, 2709–2712.

10.1021/ol4028978

Scheme 1. Discovery of Allylsilane Reaction

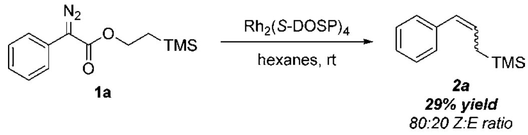
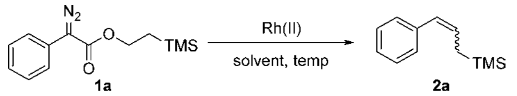


Table 1. Optimization of Allylsilane Formation[c]



entry	Rh(II)	solvent	temp	Z/E ratio[a]	yield (%)[b]
1	$Rh_2(S\text{-DOSP})_4$	$PhCF_3$	70	80:20	57
2	$Rh_2(S\text{-BTPCP})_4$	$PhCF_3$	70	74:26	45
3	$Rh_2(S\text{-PTAD})_4$	$PhCF_3$	70	83:17	42
4	$Rh_2(Oct)_4$	$PhCF_3$	70	47:53	48
5	$Rh_2(Piv)_4$	$PhCF_3$	70	48:52	58
6	$Rh_2(pfb)_4$	$PhCF_3$	70	50:50	17
7	$Rh_2(TFA)_4$	$PhCF_3$	70	51:49	25
8	$Rh_2(esp)_2$	$PhCF_3$	70	46:54	42
9	$Rh_2(TPA)_4$	$PhCF_3$	70	84:16	70
10	$Rh_2(TPA)_4$	$PhCF_3$	40	85:15	36
11	$Rh_2(TPA)_4$	cyclohexane	81	87:13	64
12	**$Rh_2(TPA)_4$**	**1,2-DCE**	**83**	**89:11**	**76**

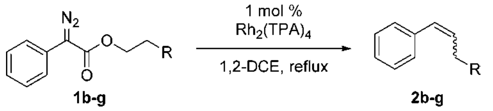
[a] Determined by ^{1}H NMR analysis of the crude reaction mixture. [b] Isolated yield of the mixture of isomers. [c] See references for preparation and structures of $Rh_2(DOSP)_4$, $Rh_2(BTPCP)_4$, and $Rh_2(PTAD)_4$.[8]

found to be 1,2-dichloroethane (1,2-DCE) at reflux (entry 12) and allylsilane **2a** was isolated in 76% yield with a *Z*/*E* ratio of 89:11.

Having established the optimal conditions, we next explored the influence of the silyl group on the reaction (Table 2). The use of bulkier alkyl silyl groups (entries 1–3) resulted in improved *Z*/*E* ratios of the products **2b**–**2d**, without decreasing of the yield. In the case of the triisopropylsilyl diazo **1d**, the allylsilane **2d** was isolated as essentially a single isomer in 82% yield. Aryl-substituted silyl groups generally did not perform as well as their alkyl-substituted counterparts (entries 4 and 5), giving **2e** and **2f** in good yields (70–80%) but without improvement of the *Z*/*E* ratio relative to **2a**. The *tert*-butyldiphenylsilyl derivative **1g**, however, resulted in the formation of allylsilane **2g** in 68% yield as a 96:4 mixture of *Z* and *E* isomers, respectively.

With the knowledge that the bulky triisopropylsilyl group is optimal for formation of *Z*-allylsilanes, we next evaluated the scope of the reaction (Scheme 2) relative to the diazo donor group. Both electron-rich (entries 1–2) and electron-poor (entries 3–4) aryl groups performed well, giving the allylsilane products in good yields (60–77%), and with good *Z*/*E* ratios (95:5 to >97:3). Halogenated aryl groups were also well tolerated (entries 5–7), giving the allylsilanes in ≥97:3 *Z*/*E* ratios and good yields (64–74%). The *Z*/*E* ratio dropped slightly with an *ortho*-chloro substituent, and allylsilane **4h** was formed in 77% yield and with a 94:6 *Z*/*E* ratio (entry 8). A 2-naphthyl aryl group was effective in this chemistry (entry 9), and **4i** was formed in 74% yield with a >97:3 *Z*/*E* ratio. It was also possible to form conjugated polyenes **4j** and **4k** by using styryldiazoacetate **3j** and phenyldienyldiazoacetate **3k** as substrates (entries 10–11) with control over alkene geometry of each alkene (93:7 to 95:5 *Z*/*E* ratio). The relatively low isolated yield (37%) of **4k** was at least partially due to product instability. The reaction could be extended to the formation of the trisubstituted allylsilane **4l**, but in this case competing side reactions were observed.[9]

Table 2. Optimization of Substrate



entry	R	product	Z/E ratio[a]	yield (%)[b]
1	$SiEt_3$	**2b**	91:9	76
2	$SiMe_2t\text{-Bu}$	**2c**	95:5	79
3	**$Si(\textit{i}\text{-Pr})_3$**	2d	**>97:3**	**82**
4	$SiMe_2Ph$	**2e**	88:12	80
5	$SiMePh_2$	**2f**	89:11	70
6	$SiPh_2\textit{t}\text{-Bu}$	**2g**	96:4	68

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture. [b] Isolated yield of the mixture of isomers.

The reaction can also be extended to form chiral allylsilanes by using esters derived from chiral alcohols. As can be seen from Scheme 3, yields and selectivities are respectable for the formation of allylsilanes **6a**–**c** (47–68% yield and 90:10 to >97:3 *Z*/*E* ratio).

Enantiomerically enriched allyl silanes can be formed by a sequence using two rhodium-catalyzed reactions (Scheme 4). The $Rh_2(S\text{-DOSP})_4$-catalyzed reaction of phenyldiazoacetate **7a** with *tert*-butyldimethylsilane results in Si–H insertion and the formation of **8a** in 88% yield and 86% ee. The stereochemistry of **8a**, and products derived from it, were tentatively assigned by comparison to previously reported results in a similar system.[6b] Reduction of **8a** with DIBAL-H gave **9a** in 89% yield. Esterification and diazo transfer produced **(*R*)-5a** in 39% yield over two steps. The $Rh_2(TPA)_4$ catalyzed conversion of **(*R*)-5a** to the allylsilane **6a** required slightly more vigorous conditions than those used for the simpler systems, but still **6a** was formed with retention of the enantioenrichment.

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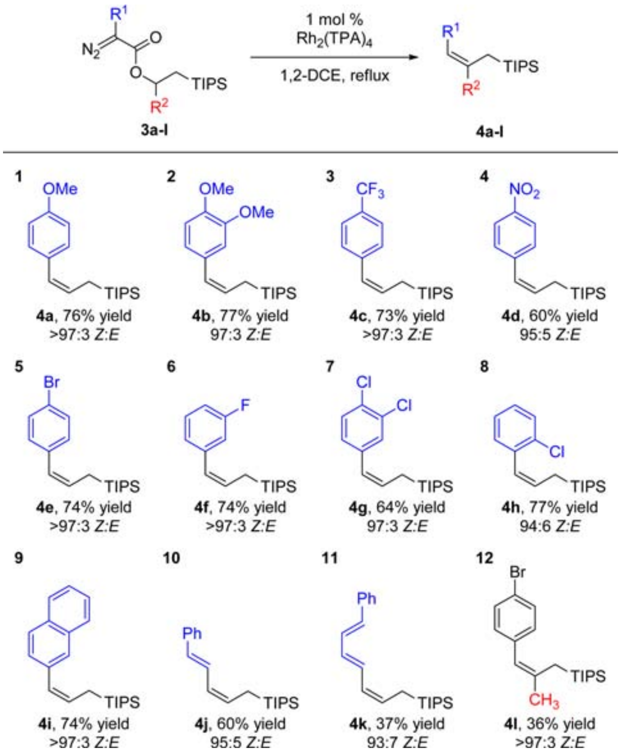
(8) (a) For DOSP: Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J.; York, N.; Forest, W.; Uni, V.; Carolina, N. *J. Am. Chem. Soc.* **1996**, *118*, 6897–6907. (b) For BTPCP: Qin, C.; Boyarskikh, V.; Hansen, J. H.; Hardcastle, K. I.; Musaev, D. G.; Davies, H. M. L. *J. Am. Chem. Soc.* **2011**, *133*, 19198–19204. (c) For PTAD: Reddy, R. P.; Lee, G. H.; Davies, H. M. L. *Org. Lett.* **2006**, *8*, 3437–3440.

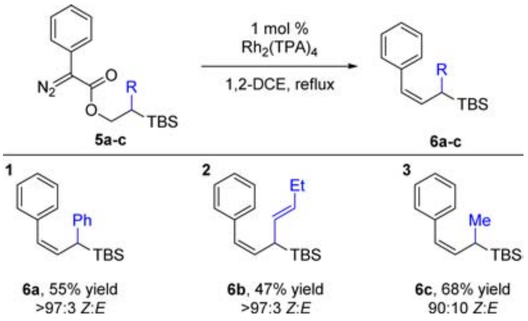
(9) Triisopropylsilylacetone was also formed, in 39% yield, presumably by a hydride abstraction mechanism.

Scheme 2. Scope of the Donor Group[a,b]



[a] Z/E ratios determined by ^1H NMR analysis of the crude reaction mixtures. [b] Yields refer to isolated yields.

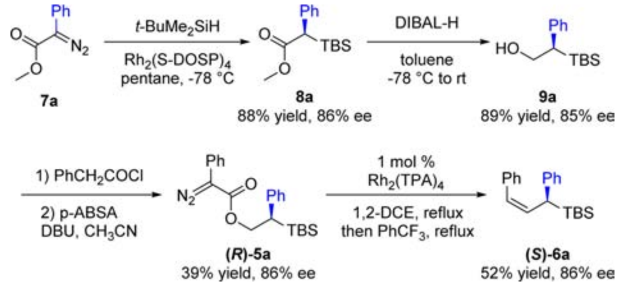
Scheme 3. Synthesis of Chiral Allylsilanes[a,b]



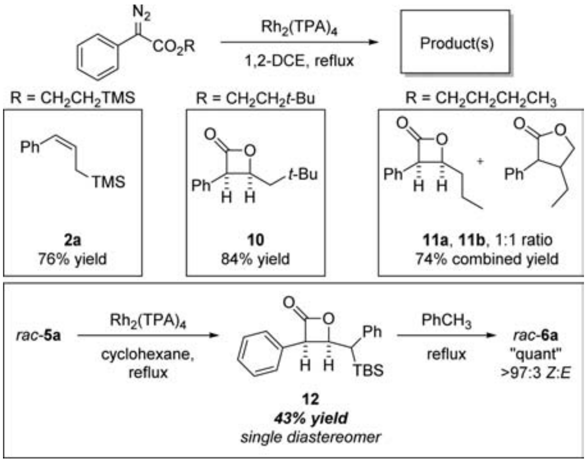
[a] Z/E ratios determined by ^1H NMR analysis of the crude reaction mixtures. [b] Yields refer to isolated yields.

In the interest of elucidating the mechanism of this transformation, we ran a series of control reactions (Scheme 5). For reference, the reaction of trimethylsilylethyl derivative **1a** to give **2a** is shown. First, to determine the effect of the silicon group, we replaced the TMS with a *tert*-butyl group. Under the standard conditions the β-lactone **10** was formed in 84% yield. β-Lactone **10** showed no signs of decomposition after 16 h at reflux in $PhCF_3$. When an *n*-Bu ester was used, however, a mixture of β-lactone **11a** and γ-lactone **11b** was formed in a 1:1 ratio. Finally, with the more highly funtionalized diazoacetate **5a**, β-lactone **12** could be isolated as a single, *cis* diastereomer. Further, when **12** was heated in toluene at reflux, it was smoothly converted to the allylsilane **6a**, as exclusively the *Z* isomer.

Scheme 4. Synthesis of Enantioenriched Allylsilane **6a**



Scheme 5. Control Reactions



From the above experiments, and other observations noted below, we propose the following conclusions: (1) *β-lactones are likely intermediates in the formation of the allylsilanes*. The isolation and characterization of **12** is the primary evidence.[10] Additionally, when nonpolar solvents are used, β-lactones can be observed in the crude mixture by ^1H NMR, though they are unstable and proved not to be isolable. (2) *The presence of the silicon is important for a facile rearrangement of the β-lactone intermediates.*[11] This is supported by the isolability and thermal stability of **10**. Since a TMS and a *t*-Bu group are similar sterically, this could be due to an electronic effect. The solvent effect mentioned above supports this as well. (3) *The rearrangement*

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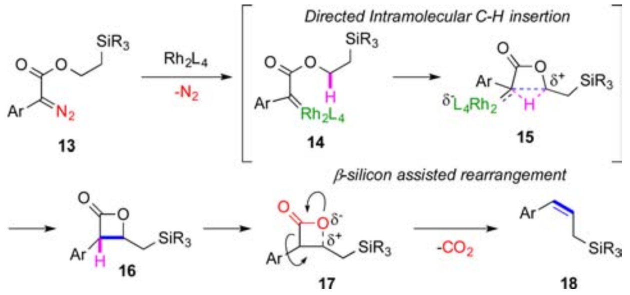
(10) Some examples of β-lactone formation by intramolecular carbenoid C−H insertion: (a) Doyle, M. P.; May, E. J. *Synlett* **2001**, 967–969. (b) Doyle, M. P.; Davies, S. B.; May, E. J. *J. Org. Chem.* **2001**, *66*, 8112–8119. (c) Balaji, B. S.; Chanda, B. M. *Tetrahedron Lett.* **1998**, *39*, 6381–6382.

(11) Rearrangements of β-lactones to give alkenes are known, though harsh conditions are required: (a) Adam, W.; Nava-Salgado, V. O. *J. Org. Chem.* **1995**, *60*, 578–584. (b) Fleming, I.; Sarkar, A. K. *J. Chem. Soc., Chem. Commun.* **1986**, 1199–1201. (c) Mulzer, J.; Pointner, A.; Chucholowski, A.; Bruntrup, G. *J. Chem. Soc., Chem. Commun.* **1979**, 52–54.

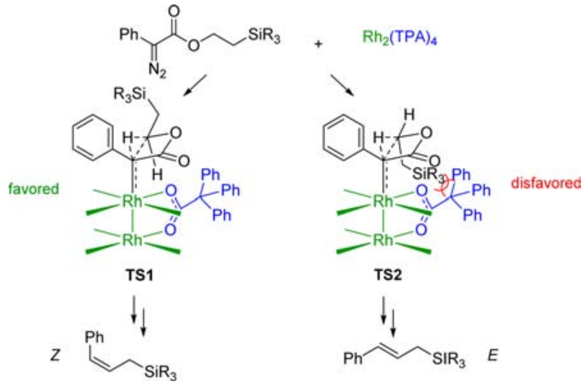
of the intermediate β-lactones is stereospecific. This is supported by the rearrangement of a single diastereomer of **12** to a single isomer of **6a** and the dramatic effect of the rhodium catalyst on the *Z*/*E* selectivity (Table 1). The stereospecific rearrangement of β-lactones is precedented in the literature as well.[11] (4) *The silicon directs the C−H insertion to the β-position.* Since **10** is formed from a bulky ester while the less crowded *n*-Bu ester leads to a mixture of **11a** and **11b**, the silicon is likely exhibiting a steric effect: directing the C−H insertion away from the more crowded α-position (and the formation of a 5-membered ring such as **11b**). Nevertheless, an electronic directing effect cannot necessarily be ruled out: The silicon could electronically disfavor C−H insertion (and the resulting build-up of positive charge character[12]) at the α position and/or favor C−H insertion β to silicon.

Scheme 6. Proposed Mechanism for Allylsilane Formation



With these observations, we propose a mechanism that occurs in three steps (Scheme 6). First, rhodium-catalyzed extrusion of nitrogen from diazo **13** generates the rhodium-carbenoid intermediate **14**. Second, the carbenoid undergoes an intramolecular C−H insertion β to the silicon, forming the intermediate β-lactone **16**.[13] Third, the silicon facilitates the polarization of the lactone C−O bond (**17**), from which the loss of CO_2 and concomitant double bond formation gives the observed allylsilane **18**.

Scheme 7. Stereochemical Rationale



With a reasonable mechanistic proposal in place, we next provide a rationale for the stereochemical outcome of this reaction (Scheme 7). As previously discussed, it is likely the diastereoselectivity of the C−H insertion step is responsible for the stereochemistry of the allylsilane product. We considered two diastereomeric transition states for this step (**TS1** and **TS2**). In transition state **TS1**, the bulky trialkylsilyl group is positioned away from the triphenylacetate ligands. In transition state **TS2**, however, the trialkylsilyl group would be expected to experience a disfavorable steric interaction with the ligands. The preferred pathway (**TS1**) ultimately leads to the observed major *Z* product.

In summary, these studies demonstrate that 2-(trialkylsilyl)-ethyl aryl- and vinyldiazoacetates are effective reagents for the synthesis of allylsilanes. With 2-(triisopropylsilyl)ethyl esters and $Rh_2(TPA)_4$ as the catalyst, *Z*-allylsilanes are produced exclusively. The reaction is considered to proceed by an intramolecular C−H insertion followed by a β-lactone rearrangement. The high selectivity and novelty of this method for the synthesis of allylsilanes is likely to be of utility to the synthetic community.

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Supporting Information Available. Full experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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(12) Hansen, J.; Autschbach, J.; Davies, H. M. L. *J. Org. Chem.* **2009**, *74*, 6555–6563.

(13) For some reviews concerning intramolecular C−H insertion, see the following, and references contained therein: (a) Doyle, M.; McKervey, M.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*; Wiley: New York, 1998. (b) Taber, D. F. In*Comprehensive Organic Synthesis*; Pattenden, G., Ed.; Pergamon Press: Oxford, U.K., 1991; Vol. 3, Chapter 4.2. (c) Davies, H. M. L.; Dai, X. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier, 2007; pp 167−212.